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Novel C1-Bridged Bisboronate Derivatives by Insertion of Diazoalkanes into Bis(pinacolato)diborane(4)[⊥]

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The insertion reaction of bis(pinacolato)diborane(4) [$(Me_4C_2O_2)BB(O_2C_2Me_4)$, **1**] with various diazoalkanes provided novel representatives of a new class of substituted C1-bridged bis(pinacolato)diborane(4) derivatives **5a**, **5b**, **5c**, and **5d** in a range of 75−78% isolated yields. The reaction was efficiently catalyzed by $Pt(PPh_3)_4$ in toluene at 110 °C. Single-crystal X-ray diffraction, GCMS, and NMR multinuclear spectroscopies fully confirmed the structure and configuration of the new compounds. Crystals of **5a** and **5c** are centrosymmetric, while those of **5d** are chiral. **5b** crystallized with a somewhat unusual *Fdd*2 space symmetry. While its crystals are noncentrosymmetric, they contain mirror-related species. The degree of puckering of the five-membered C_2O_2B rings, as well as the dihedral angles between the mean planes of these rings, vary from one compound to another and to some extent from one ring to another within the same compound.

Introduction

Bidentate Lewis acids are gaining increased utilization in synthetic transformations and as complexation reagents since it is recognized that they tend to increase reaction selectivity and substrate activation by acting in concert.[1] They have been shown to be effective in the activation of organic reactions,[2] catalysis,[3] and molecular recognition[4] and for enhanced activation of basic substrates and the selective binding of anions. These effects have been demonstrated with aluminum,[5] mercury,[6] titanium,[7] tin,[8] boron,[9] and indium.[10] Of particular interest to us are C1-bridged 1,1-dibora reagents. In addition to the above-mentioned uses, 1,1-dibora reagents can also undergo interesting chemical transformations. Thus, 1,1-diboraalkanes react with 2 molar equiv of methyl- or butyllithium to furnish 1-borato-1-lithio alkanes, which can be reacted with carbon dioxide to yield alkylmalonic acids.[11] The use of 1 equiv of *n*-BuLi produces 1,1-lithioboranes, which react with aldehydes and ketones to form alkenes.[12] Sequential reaction of the 1,1-lithioboranes is also possible.[13] Oxidation of 1,1-diboraalkanes with H_2O_2 in acidic medium proceeds very smoothly, providing aldehydes in good yield.[14] Heating 1,1-bis(dialkylbora)-3-chloropropanes with sodium tetraethylborate induces cyclization, forming cyclopropyldialkylboranes.[15] Treatment of the dihydroborated product of 3-butyn-1-ol with methyllithium leads to the formation of a cyclobutylborane.[16] 1,1-Bis(dimethoxybora)alkanes react with mercuric chloride to form, 1,1-bis(chloromercurio)alkanes.[17] C1-bridged 1,1-dibora reagents are usually obtained by

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[⊥] This paper is dedicated to Professor Herbert C. Brown, a pioneer in organoboranes and their uses in synthesis, on the occasion of his 90th birthday.

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(1) Piers, W. E.; Irvine, G. J.; Williams, V. C. *Eur. J. Inorg. Chem.* **2000**, 2131.

(2) Maruoka, K. *Catal. Today* **2001**, *66*, 33.

(3) Jia, L.; Yang, X.; Stern, C.; Marks, T. J. *Organometallics* **1994**, *13*, 3755.

(4) (a) Wuest, *Acc. Chem. Res.* **1998**, *32*, 81. (b) Gabbaï, F. P.; Schier, A.; Riede, J.; Hynes, M. J. *Chem. Commun.* **1998**, 897. (b) Williams, V. C.; Piers, W. E.; Clegg, W.; Elsegood, M. R. J.; Collins, S.; Marder, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 3244. (c) Uhl, W.; Hannemann, F.; Saak, W.; Wartchow, R. *Eur. J. Inorg. Chem.* **1998**, 921.

(5) (a) Sharma, V.; Simard, M.; Wuest, J. D.; *J. Am. Chem. Soc.* **1992**, *114*, 7931. (b) Kaul, F. A. R.; Tschinkl, M.; Gabbaï, F. P. *J. Organomet. Chem.* **1997**, *539*, 187.

(6) (a) Wuest, J. D.; Zacharie, B. *Organometallics* **1985**, *4*, 410. (b) Schmidbaur, H.; Öller, H.-J.; Wilkinson, D. L.; Huber, B. *Chem. Ber.* **1989**, *122*, 31. (c) Tikhonova, I. A.; Dolgushin, F. M.; Yanovsky. A. I.; Struchkov, Yu.; Gavrilova, A. N.; Saitkulova, L. N.; Shubina, E. S.; Epstein, L. M.; Furin, G. G.; Shur, V. B. *J. Organomet. Chem.* **1996**, *508*, 271. (d) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *Organometallics* **1987**, *6*, 153. (e) Vaugeois, J.; Simard, M.; Wuest, J. D. *Organometallics* **1998**, *17*, 1208.

(7) Asao, N.; Kii, S.; Hanawa, H.; Maruoka, K. *Tetrahedron Lett.* **1998**, *39*, 3729.

(8) Newcomb, M.; Homer, J. H.; Blanda, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 7878. (b) Jurkschat, K.; Kuivila, H. G.; Liu, S.; Zubieta, J. A. *Organometallics* **1989**, *8*, 2755. (c) Altmann, R.; Jurkschat, K.; Schürmann, M. *Organometallics* **1998**, *17*, 5858, and references cited.

(9) (a) Shriver, D. F.; Biallas, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 1078. (b) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 5027. (c) Katz, H. E. *J. Am. Chem. Soc.* **1986**, *108*, 7640.

(10) Tschinkl, M.; Schier, A.; Riede, J.; Gabbaï, F. P. *Inorg. Chem.* **1997**, *36*, 5706.

(11) Cainelli, G.; Dal Bello, G.; Zubiani, G. *Tetrahedron Lett.* **1965**, 3429.

(12) Cainelli, G.; Dal Bello, G.; Zubiani, G. *Tetrahedron Lett.* **1966**, 4135.

(13) Zweifel, G.; Arzoumanian, H. *Tetrahedron Lett.* **1966**, 2535.

(14) (a) Mikhailov, B. M.; Aronovich, P. M.; Kiselev, V. G. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1968**, 146. (b) Aronovich, P. M.; Bogdanov, V. S.; Mikhailov, B. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1969**, 362. (c) Matteson, D. S.; Shdo, J. G. *J. Org. Chem.* **1964**, *29*, 2742.

(15) Binger, P.; Köster, R. *Angew. Chem.* **1962**, *74*, 652.

(16) Brown, H. C.; Rhodes, S. P. *J. Am. Chem. Soc.* **1969**, *91*, 4306.

(17) Larock, R. C. *J. Organomet. Chem.* **1973**, *61*, 27.

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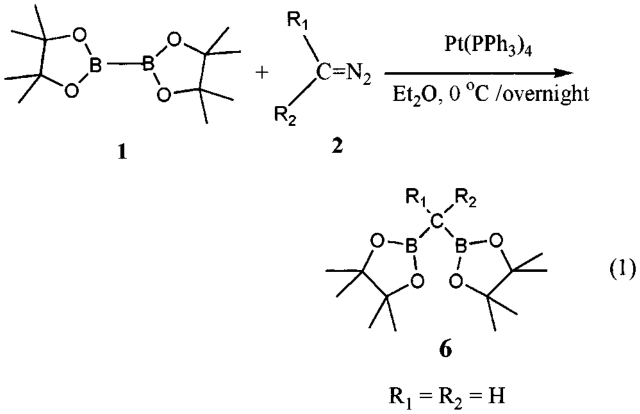
hydroboration of terminal alkynes with a hydroborating reagent. The hydroborating reagent of choice is 9-BBN.[18] Use of diborane leads to mixtures of products.[19a] $(C_2H_4O_2B)_2C(Et)_2$ was obtained from lithiodeboronation of $[(MeO)_2B]_4C$, alkylation with ethyl iodide, and transestrification with ethylene glycol.[19b] Alkylation of the lithiated 1,1-diboryl esters is another method that was used by Matteson and Moody, to get such boronic esters.[19c] Dihydroboration of internal alkynes also leads to mixtures and is not practical.[19d,e] Thermal isomerization of the products obtained from hydroboration of dienes with diborane leads to a 1,1-bis(bora)alkanes.[20] Preperation of pinacol methylenediboronate was previously reported by Castle and Matteson.[21a] For higher homologues, the method of hydroboration of alkynes with $HBCl_2$ used by Matteson and Soundararjan may be the most efficient route to many compounds of this class.[21b,c] We have recently reported a new reaction involving bis(pinacolato)diborane(4), **1** (eq 1). Treatment of **1** with an etheral solution of diazomethane in the presence of $Pt(PPh_3)_4$ resulted in the high-yield synthesis of **6** ($R_1 = R_2 = H$).[21d]



(1)

This is a new carbenoid insertion reaction into the B−B bond.[22] The reaction possesses the possibility of preparing C1-bridged bis-boronates with a quaternary carbon atom, and it is the subject of our present paper.

Results and Discussion

Reaction of bis(pinacolato)diborane(4) with diphenyl diazomethane, 1-diazo-1,2,3,4-tetrahydronaphthalene, methyl phenyl diazomethane, and 2-methoxyphenyl methyl diazomethane in the presence of a catalytic amount of $Pt(PPh_3)_4$ (3 mol %) in toluene at 110 °C overnight gave the desired insertion products of substituted C1-bridged bis(pinacolato)diborane(4) derivatives **5a**, **5b**, **5c**, and **5d** with evolution of N_2 gas (Scheme 1).

No detectable amount of insertion product was observed without catalyst, but the reaction was efficiently catalyzed by $Pt(PPh_3)_4$. The desired products **5a**, **5b**, **5c**, and **5d** were produced in an isolated yields of 78%, 75%, 76%, and 75%, respectively. The reaction initially requires a Pt(0) complex, which we believe generates the active Pt(II) catalytic species. The reaction is apparently similar to other reactions catalyzed by transition metals involving oxidative addition of B−H,[23] Si−Si,[24] Sn−Sn,[25] and Si−Sn[26a] compounds to low-valent transiton-metal complexes, the key step in the catalytic diboration,[26b,c] hydroboration,[27] and addition of disilanes,[28] distannanes,[29] or silylstannanes[30] to alkenes and alkynes.

The present insertion reaction shown in (Scheme 1) may involve (a) B−B bond activation by oxidative addition of **1** to the platinum(0) complex to form a bis(boryl) platinum(II) intermediate **3**, (b) the insertion of a generated carbene from various diazo methanes to the B−Pt bond to form **4**, and finally (c) the reductive elemination to give **5** (Figure 1).

The structure of bis(boryl) platinum(II) intermediate **3** was confirmed by Ishiyama et al.,[31] who obtained a single crystal of **3** suitable for X-ray analysis in an 82% yield by treatment of $Pt(PPh_3)_4$ with 20 equiv of **1** in hexane at 80 °C for 2 h, followed by recrystallization from hexane/toluene (eq 2).

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(18) Brown, H. C.; Scouten, C. G.; Liotta, R. *J. Am. Chem. Soc.* **1979**, *101*, 96.

(19) (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 3834. (b) Matteson, D. S.; Thomas, J. R. *J. Organomet. Chem.* **1970**, *24*, 263. (c) Matteson, D. S.; Moody, R. *J. Organometallics* **1982**, *1*, 20. (d) Pasto, D. J. *J. Am. Chem. Soc.* **1964**, *86*, 3039. (e) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 291.

(20) Negishi, B.; Burke, P. L.; Brown, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 7431. (b) Brown, H. C.; Negishi, E.; Gupta, S. K. *J. Am. Chem. Soc.* **1970**, *92*, 2460.

(21) (a) Castle, R. B.; Matteson, D. S. *J. Organomet. Chem.* **1969**, *20*, 19. (b) Soundararajan, R.; Matteson, D, S. *J. Org. Chem.* **1990**, *55*, 2274. (c) Matteson, D. S.; Soundararajan, R. *Organometallics* **1995**, *14*, 4157. (d) Abu Ali, H.; Goldberg, I.; Srebnik, M. *Organometallics* **2001**, *20*, 3962.

(22) For carbenoid insertion into B−C bonds: Vasella, A.; Wenger, W.; Rajamannar, T. *Chem. Commun.* **1999**, 2215.

(23) (a) Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Can. J. Chem.* **1993**, *71*, 930. (b) Westcott, S. A.; Tayler, N. J.; Marder, T. B.; Baker, R. T.; Jones, N. J.; Calabrese, J. C. *J. Chem. Soc., Chem Commun.* **1991**, 304. (c) Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Tayler, N. J.; Williams, I. D.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, *112*, 9399. (d) Knorr, J. R.; Merola, J. S. *Organometallics* **1990**, *9*, 3008. (e) Kono, H.; Ito, K.; Nagia, Y. *Chem. Lett.* **1975**, 1095. (f) Churchil, M. R.; Hackbarth, J. J.; Davison, A.; Traficante, D. D.; Wreford, S. S. *J. Am. Chem. Soc.* **1974**, *96*, 4041.

(24) (a) Yamashita, H.; Kobayashi, T. A.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447. (b) Eaborn, C.; Griffiths, R. W.; Pidock, A. *J. Organomet. Chem.* **1982**, *225*, 331. (c) Glockling, F.; Houston, R. E. *J. Organomet. Chem.* **1973**, *50*, C31−C32. (d) Schmid, G.; Balk, H. J. *Chem. Ber.* **1970**, *103*, 2240.

(25) (a) Weichmann, H. *J. Organomet. Chem.* **1982**, *238*, C49−C52. (b) Akhtar, M.; Clark, H. C. *J. Organomet. Chem.* **1970**, *22*, 233.

(26) (a) Murakami, M.; Yoshida, T.; Kawanami, S.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6408. (b) Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Organometallics* **1996**, *15*, 5137. (c) Iverson, C. N.; Smith, M. R. *Organometallics* **1996**, *15*, 5155.

(27) (a) Gridnev, I. D.; Miyaura, N.; Suzuki, A. *Organometallics* **1993**, *12*, 589. (b) Burgess, K.; Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350. (c) Westcott, S. A.; Blom, H. B.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863. (d) Evans, D. A.; Fu, G. C.; Anderson, B. A. *J. Am. Chem. Soc.* **1992**, *114*, 6679. (e) Satoh, M.; Nomoto, Y.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1989**, *30*, 3789. (f) Hyashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426. (g) Wilczynsky, R.; Sneddon, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 2857.

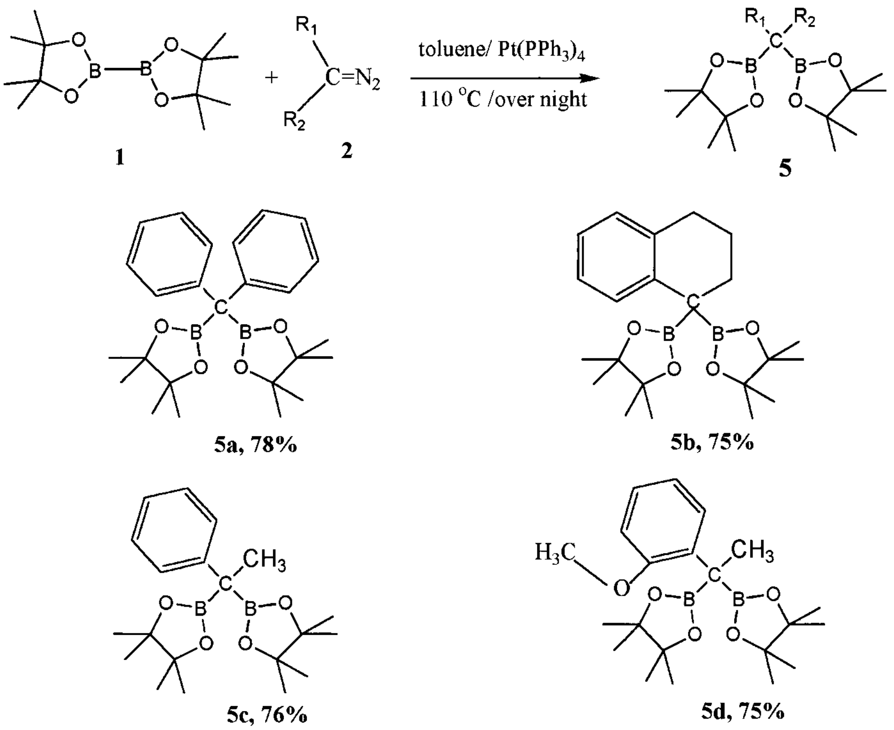
(28) (a) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237. (b) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Anderson, P. G.; Ito, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6487. (c) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948. (d) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagia, Y. *J. Organomet. Chem.* **1980**, *186*, 51.

(29) (a) Michell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1986**, *304*, 257. (b) Killing, H.; Michell, T. N. *Organometallics* **1984**, *3*, 1318. (c) Michell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1983**, *241*, C45−C47.

(30) (a) Murakami, M.; Amii, H.; Takizawa, N.; Ito, Y. *Organometallics* **1993**, *12*, 4223. (b) Tsuji, Y.; Obora, Y. *J. Am. Chem. Soc.* **1991**, *113*, 9368. (c) Michell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868. (d) Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561.

(31) Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713.

Scheme 1. Insertion Reaction of Diazoalkanes with Bis(pinacolato)diborane(4)



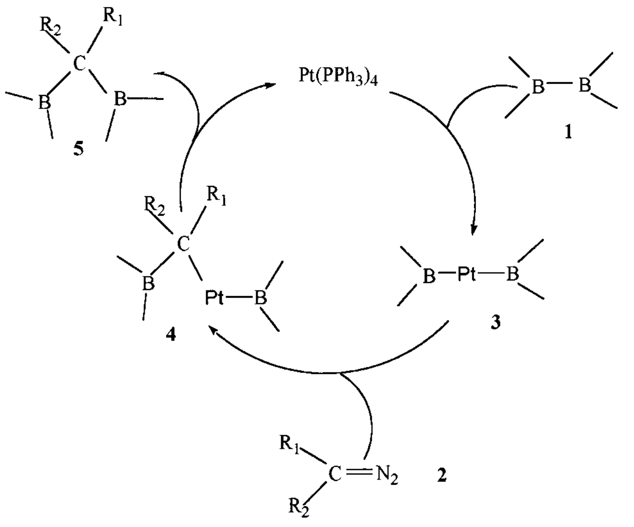
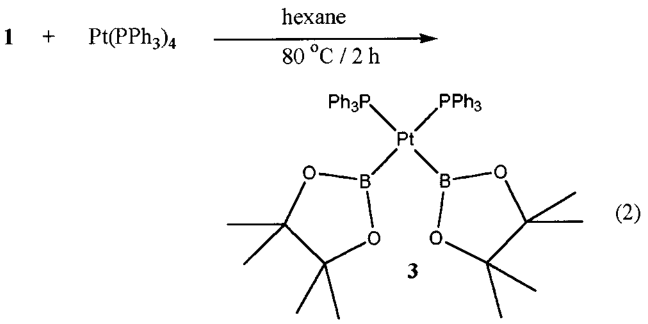


Figure 1. Suggested catalytic cycle for the insertion reaction.



The new compounds have been characterized by ^{1}H, ^{13}C, and ^{11}B NMR, GC/MS, elemental analysis, and single-crystal X-ray structure determination. The compounds are all monomers in the solid state. In the crystalline form they are air-stable. Crystals of **5a** and **5c** (centrosymmetric), as well as of **5b** (noncentrosymmetric), are achiral; those of **5d** are chiral. This variation may be due to the synthesis or to the asymmetric substituents used in **5b** and **5d**. In solution, the compounds are stable, and their solubility in common organic solvents ranges from quite good (alkanes) to excellent (in aromatic solvents, chlorinated solvents, and ethers). This reflects the monomeric structure of the compounds. In the ^{1}H NMR spectra (CDCl$_3$) of compounds **5c** and **5d** the methyl protons appear upfield compared to their parent keto and diazo compounds. The methyl resonances are found at 1.45 ppm for **5c** and 1.35 ppm for **5d**. In **5d** the methoxy protons also appear upfield at 3.78 ppm. The resonances of the aromatic protons for **5a**, **5b**, **5c**, and **5d** are shifted upfield and observed at 7.27 ppm (m, 10H, Ph) for **5a**, at 6.97 ppm (m, 4H, Ph) for **5b**, at 7.28 ppm (m, 5H, Ph) for **5c**, and at 6.78 ppm (dd, 1H, CH, $^3J_{H-H}$ = 7.8, $^4J_{H-H}$ = 0.9 Hz), 6.85 ppm (dt, 1H, CH, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 1.2 Hz), 7.10 ppm (dt, 1H, CH, $^3J_{H-H}$ = 8.01, $^4J_{H-H}$ = 2.1 Hz), 7.24 ppm (dd, 1H, CH, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 1.5 Hz) for **5d**. The pinacolato methyl resonances for **5c** and **5d** are observed as a pair of singlets at 1.22 ppm (s, 12H) and 1.23 ppm (s, 12H) for **5c** and at 1.26 ppm (s, 12H) and 1.27 ppm (s, 12H) for **5d**. This could be explained as follows: If we assume fast rotation about the B−C bonds on the NMR time scale, the methyl groups **a** and **b** in the figure below are diastereotopic when $R_1 \neq R_2$, and two resonances are expected.

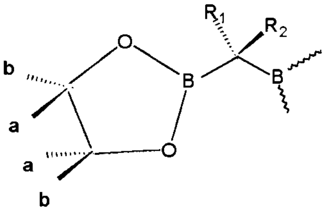


Table 1. Selected Parameters of Molecular Geometry

	5a[a]	**5b**	**5c**	**5d**	average
	1.365(2)	1.369(4)	1.368(2)	1.371(2)	1.371
B-O bond lengths, Å	1.372(2)	1.376(4)	1.370(2)	1.374(2)	
		1.371(4)	1.368(2)	1.369(2)	
		1.373(4)	1.373(2)	1.373(2)	
B−C(sp^3) bond lengths, Å	1.587(2)	1.586(4)	1.587(2)	1.589(2)	1.583
		1.574(5)	1.582(2)	1.578(2)	
O−B−O bond angles, deg	113.4(1)	112.8(3)	113.4(1)	113.0(1)	113.1
		112.8(3)	113.3(1)	112.8(2)	
	124.1(1)	120.2(3)	123.5(3)	123.3(1)	123.4
O−B−C bond angles, deg	122.3(1)	126.9(3)	123.7(1)	122.8(1)	
		123.5(3)	123.7(1)	124.2(1)	
		123.5(3)	121.9(1)	123.0(2)	
puckering of C_2O_2B rings[39]					
q_2, Å	0.269(1)	0.671(3)	0.284(1)	0.219(2)	
		0.748(3)	0.307(1)	0.255(2)	
ϕ_2, deg	90.1(2)	−152.6(2)	93.1(2)	−92.6(4)	
		−157.8(2)	−91.1(2)	91.4(4)	
dihedral angles between the two C_2O_2B rings, deg	46.3(1)	119.5(1)	83.5(1)	79.3(1)	

[a] Molecules are located on 2-fold axes of crystallographic rotational symmetry.

Since the differences in chemical shifts are only 0.01 ppm, perhaps the resonances are indistinguishable in **5b**. In compound **5a**, where $R_1 = R_2 = Ph$, a single resonance is expected. The signals of the aliphatic protons in the tetralone moiety in **5b** are also shifted up and observed at 1.73 ppm (t, 2H, CH_2, $^3J_{H-H} = 6$ Hz), 1.93 ppm (m, 2H, CH_2 , $^3J_{H-H} = 6.2$ Hz), and 2.74 ppm (t, 2H, CH_2 , $^3J_{H-H} = 6.2$ Hz). The pronounced upfield shifts in the ^1H and ^{13}C NMR spectra of **5a**, **5b**, **5c**, and **5d** are due to the close proximity of the substituents to two boron atoms instead of oxygen and nitrogen atoms in the parent keto and diazo compounds. The assignment of the ^{13}C NMR spectra ($CDCl_3$) is also straightforward except for the central carbon atom, which cannot be detected due to the quadrupole effect of the closely attached boron atoms. Chemical shifts and coupling constants (see Experimental Section) in the ^1H, ^{13}C, and ^{11}B NMR spectra are comparable with those found in the literature for boronic acid esters.[32−34] Mass spectra for **5a**, **5b**, and **5c** show monomeric molecular ion $(M)^+$ peaks, respectively, at *m*/*e* values of 420, 384, and 358 mass units, while **5d** shows a molecular ion $(M - CH_3)^+$ peak at an *m*/*e* value of 373 mass units. In all cases the most abundant ion was at an *m*/*e* value of 83 mass units and a prominent fragment at $(M - 100)^+$ mass units.

Crystallography. The molecular structures of **5a**, **5b**, **5c**, and **5d** were determined by single-crystal X-ray diffraction. The low-temperature diffraction experiments of the four different derivatives (which contain seven crystallographically independent units of the boronic ester moiety) at similar conditions allowed precise determination of the covalent parameters around the boron atom. The results of the diffraction analysis, crystal data, and details of the structure determination are shown in Figures 2, 3, 4, and 5, and the data are summarized in Tables 1 and 2. The molecular structures of **5a**, **5b**, **5c**, and **5d** consist of a slightly distorted tetrahedral geometry for the central bridged carbon atom, for which the significant bond angles and bond lengths are summarized in Table 1. The average B−C(sp^3) bond lengths of 1.583 Å and the average B−O bond lengths of 1.371 Å are closely similar to the previously reported B−C bond lengths (1.575(5)−1.589(5) Å) and B−O bond lengths (1.364(9)−1.370(7) Å) in boronic acid esters.[32−35] The coordination at B(1) or B(2) is distorted trigonal planar with O−B−O average bond angles of 113.1° and O−B−C average bond angles of 123.4° and is in agreement with previously reported boronic esters.[35−37] The dioxaborolane rings in **5a**, **5b**, **5c**, and **5d** are slightly distorted to release the steric repulsion between the vicinal methyl groups in contrast to the almost planar structure of bis(pinacolato)diborane(4) and bis(catecolato)diborane(4).[36,37] The

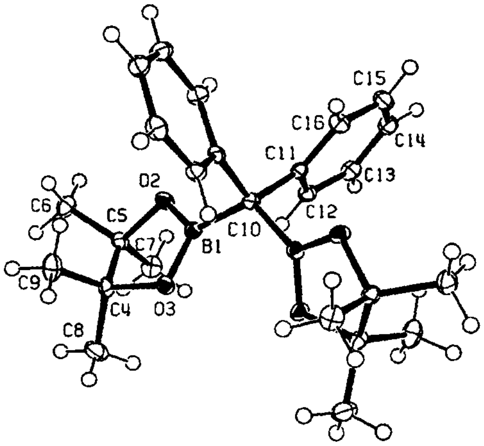


Figure 2. View of the molecular structure of **5a**, showing the atom-numbering scheme. Ellipsoids represent thermal displacement parameters at the 50% probability level. The molecules are located in the crystal on 2-fold symmetry axes. Selected bond distances (Å) and angles (deg): B(1)−C(10) = 1.5873(15), C(10)−C(11) = 1.5397(14), B(1)−O(2) = 1.3715(15), B(1)−O(3) = 1.3649(15), O(3)−B(1)−O(2) = 113.44(10), B(1)−O(2)−C(5) = 107.1(9), B(1)−C(10)−B(1) = 113.99(13), B(1)−C(10)−C(11) = 112.76(13), C(11)−C(10)−C(11) = 114.15(13).

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(32) Hyslop, A. M.; Kellett, M. A.; Iovine, P. M.; Therien, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 12676.

(33) Grigsby, W. J.; Power, P. P. *Chem. Commun.* **1996**, 2235.

(34) Zheng, B.; Deloux, L.; Skrzypczak-Jankun, E.; Cheesman, B. V.; Pereira, S.; Srebnik, M.; Sabat, M. J. *J. Mol. Struct.* **1996**, *374*, 291.

(35) Brauer, D. J.; Machnitzki, P.; Nickel, T.; Stelzer, O. *Eur. J. Inorg. Chem.* **2000**, 65.

(36) Clegg, W.; Elsegood, M. R. J., Lawlor, F. J.; Norman, N. C.; Picket, N. L.; Robins, E. G.; Scott, A. J. *Inorg. Chem.* **1998**, *37*, 5289.

(37) Nöth, H. *Z. Naturforsch.* **1984**, *39b*, 1463.

Table 2. Crystal Data and Structure Refinement for 5a, 5b, 5c, and 5d

	5a[a]	**5b**	**5c**	**5d**[b]
formula	$C_{25}H_{34}B_2O_4$	$C_{22}H_{34}B_2O_4$	$C_{20}H_{32}B_2O_4$	$C_{21}H_{34}B_2O_5$
fw	420.14	384.11	358.08	388.10
habit	prisms	prisms	prisms	plates
color	colorless	colorless	colorless	colorless
temp, K	110(2)	110(2)	110(2)	110(2)
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
cryst size, mm	0.25 × 0.20 × 0.10	0.35 × 0.25 × 0.20	0.25 × 0.20 × 0.20	0.45 × 0.25 × 0.15
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$C2/c$	$Fdd2$	$P2_1/c$	$P2_1$
a, Å	12.4680(2)	53.9430(3)	13.0510(2)	9.1980(2)
b, Å	14.3490(3)	10.3370(3)	14.5220(2)	9.4150(2)
c, Å	14.2030(3)	15.7610(6)	12.4110(2)	13.5900(4)
α, deg	90.00	90.00	90.00	90.00
β, deg	109.57	90.00	117.25	106.38
γ, deg	90.00	90.00	90.00	90.00
V, Å^3	2394.16(8)	8788.50(4)	2091.25(5)	1129.12(5)
Z	4	16	4	2
d_{calcd}, g cm^{-3}	1.166	1.161	1.137	1.142
F(000)	904	3328	776	420
μ, mm^{-1}	0.076	0.076	0.075	0.078
2θ range, deg	0−56	0−50	0−56	0−56
no. of unique reflns	3854	1920	4834	4537
no. of restraints	0	1	0	1
hkl limits	0,16/0,18/−18,17	−51,51/0,12/0,18	−17,15/−17,0/0,16	−10,10/−11,11/−18,18
no. of variables	145	266	244	263
no. of reflns with [$I > 2\sigma(I)$]	2273	1698	3964	3943
final [c]R indices [$I > 2\sigma(I)$]				
R1	0.042	0.03	0.041	0.038
wR2	0.114	0.098	0.104	0.104
max and min peak, e Å^{-3}	0.349 and −0.261	0.556 and −0.197	0.315 and −0.231	0.185 and −0.185
GOF	1.02	1.06	1.00	0.98

[a] Molecules are located on 2-fold axes of crystallographic rotational symmetry. [b] Chiral structure. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

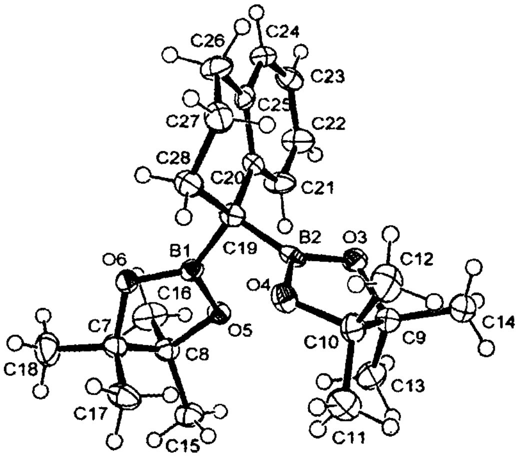

Figure 3. View of the molecular structure of **5b**, showing the atom-numbering scheme. Ellipsoids represent thermal displacement parameters at the 50% probability level. Selected bond distances (Å) and angles (deg): B(1)−C(19) = 1.586(4), C(19)−C(20) = 1.530(4), B(2)−O(4) = 1.371 (4), B(1)−O(6) = 1.369(4), O(4)−B(2)−O(3) = 112.8(3), B(2)−O(3)−C(9) = 106.4(2), B(1)−C(19)−B(2) = 101.3(2), B(1)−C(19)−C(28) = 108.4(2), C(20)−C(19)−C(28) = 111.7(2).

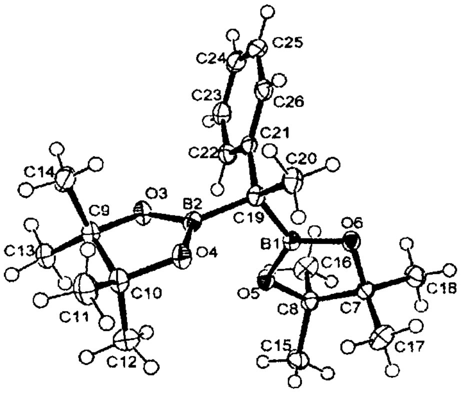

Figure 4. View of the molecular structure of **5c**, showing the atom-numbering scheme. Ellipsoids represent thermal displacement parameters at the 50% probability level. Selected bond distances (Å) and angles (deg): B(1)−C(19) = 1.5868(17), C(19)−C(21) = 1.5352(16), C(19)−C(20) = 1.5483(15), B(2)−O(4) = 1.3727 (16), B(1)−O(6) = 1.3675-(15), O(4)−B(2)−O(3) = 113.25(10), B(2)−O(3)−C(9) = 106.65(9), B(1)−C(19)−B(2) = 109.23(9), B(1)−C(19)−C(20) = 108.83(9), C(20)−C(19)−C(21) = 113.09(10).

observed bond angles in **5a**, O(3)−B(1)−O(2) 113.44°, B(1)−O(2)−C(5) 107.1°, B(1)−O(3)−C(5) 107.2°, and O(3)−C(4)−C(5) 102.1°, are also similar to those observed for **5b**, **5c**, and **5d**. The degree of puckering of the five-membered C_2O_2B rings, as well as the dihedral angles between the mean planes of these rings, vary from one compound to another and to some extent from one ring to another within the same compound, Table 1. This can be attributed mainly due to the different intramolecular steric constraints imposed by the substituents on the central carbon. The degree of ring puckering was quantitavely defined by Cremer and Pople[38] and represented by the ring-puckering coordinates q_m (Å) and ϕ_m (deg), where q_m is a puckering amplitude ($q_m \geq 0$), ϕ_m is a phase angle describing various kinds of puckering ($0 \leq \phi_m < 2\pi$), and $m = 2, 3, ..., (N - 1)/2$, where m is the number of coordinates and N is the number of atoms in the ring. Thus, for **5a−d** $m = 2$. The largest puckering of the C_2O_2B rings was observed in the mostly constrained tetralone derivative

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(38) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.

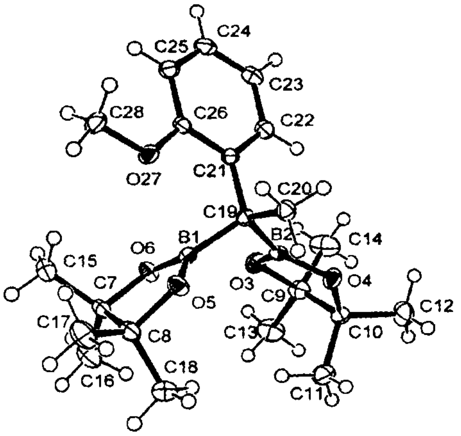

Figure 5. View of the molecular structure of **5d**, showing the atom-numbering scheme. Ellipsoids represent thermal displacement parameters at the 50% probability level. Selected bond distances (Å) and angles (deg): B(2)−C(19) = 1.578(2), C(19)−C(21) = 1.531(2), C(19)−C(20) = 1.548(2), B(1)−O(6) = 1.371 (2), B(2)−O(3) = 1.369(2), O(5)−B(1)−O(6) = 112.98(14), B(1)−O(6)−C(7) = 107.89(12), B(1)−C(19)−B(2) = 103.81(13), B(2)−C(19)−C(20) = 111.07(13), C(20)−C(19)−C(21) = 108.10(13).

5b ($\phi_2 = -152.6°, -157.8°$ and $q_2 = 0.671, 0.748$ Å). For compounds **5a**, **5c**, and **5d** the ϕ_2 values (90.1°, 93.1°, −92.6°), respectively, are close to the value (90°) appropriate to one of the twist forms. This twist form seems to be the most stable conformation for oxalane and many compounds containing five-membered rings.[39] The q_2 values for **5a**, **5c**, and **5d** are also close to those reported in the literature for many such rings which lie in a narrow range[39] (near 0.35 Å).

Compound **5b** crystallized in the somewhat unusual $Fdd2$ space group symmetry (common to only about 0.4% of organic crystal structures). While these crystals are noncentrosymmetric, they contain equal amounts of mirror-related species. On the other hand, compound **5d** formed chiral crystals in the space group $P2_1$ (common to about 6% of organic crystal structures) rather than in $P2_1/c$ (of about 36% frequency) as its analogous **5c** derivative. This could be attributed to the additional asymmetry introduced into the molecular framework by the methoxy substituent.

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere using vacuum line and glovebox techniques. Solvents were purified by distillation from appropriate drying agents under a nitrogen atmosphere. Starting materials were purchased from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution with a Varian Unity spectrometer (300 or 75 MHz) using Me_4Si as an internal standard. ^{11}B NMR spectra were also recorded in $CDCl_3$ solution with a Varian Unity spectrometer (96 MHz) using $BF_3{\cdot}OEt_2$ as an external standard. GC/MS analyses were performed on an HP GCMS instrument (Model GCD PLUS), with an EI detector and a 30 m methyl silicone column.

Diboron Reagent. Bis(pinacolato)diborane(4) was prepared from tetrakis(pyrrolidino)diborane(4) by Wurtz coupling of bis(pyrrolidino)bromoborane and then obtained by solvolysis of tetrakis(pyrrolidino)diborane(4) with 2 equiv of pinacol in benzene solution at room temperature.[40]

Diazoalkanes were prepared from the corresponding ketones and hydrazones according to literature procedures.[41−44]

Hydrazones were obtained by refluxing the ketones (2 g) and hydrazine hydrate (2 g) in 2 mL of *n*-butanol for 2 h. The hydrazone that usually separated out on cooling was filtered off and washed with hexane and can be used directly after drying for the preparation of the diazoalkane.

General Procedure for the Preparation of Diazoalkanes. Pieces of sodium (1 g, 44 mmol) were slowly added to 40 mL of dry ether with stirring under a nitrogen atmosphere. Stirring was continued, and the contents were heated under reflux for 2 h. A solution of the hydrazone (2 g) in dry ether (75 mL) was added dropwise. The reaction mixture was stirred and heated under reflux overnight. Oxygen gas was passed through for 15 min, and the mixture was allowed to cool. Unreacted pieces of sodium were removed by filtration. The ethereal solution was treated with 10% aq. ammonium chloride, and the organic layer was washed twice with water and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator, and the residue was dissolved in *n*-hexane (25 mL) and filtered to remove any unreacted hydrazones. The solid products were crystallized from *n*-hexane.

General Procedure for the Preparation of (pinacolato)$_2$BC(R$_1$R$_2$)B by Diazoalkane Insertion. A dry, nitrogen-flushed 50 mL flask equipped with a magnetic stirring bar was charged with $Pt(PPh_3)_4$ (74.7 mg, 0.06 mmol) and bis(pinacolato)diborane(4) (508 mg, 2 mmol); 15 mL of toluene was then added to the mixture. The diazoalkane (2.1 mmol) dissolved in 10 mL of toluene was then added. After the mixture was stirred overnight at 110 °C, the toluene was removed under vacuum. The residue was extracted with pentane, which was then removed under vacuum, and the product was purified by silica gel column chromatography with 8% ether/petroleum ether as eluent to give the product as colorless crystals.

$[(Me_4C_2O_2)BC(C_6H_5)_2B(O_2C_2Me_4)]$, 5a: 78% (0.66 g) yield, mp 125 °C. ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 24H, CH_3), 7.27 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.50 (CH_3), 83.56 (CCH_3), 124.86 (para CH), 127.81 (ortho or meta CH), 130.45 (ortho or meta CH), 143.63 (ipso), (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ 31.82. Anal. Calcd for $C_{25}H_{34}O_4B_2$: C, 71.49; H, 8.16. Found: C, 71.06; H, 8.09. MS (EI) *m*/*z* (%): 420 (M^+, 4.5), 405 (0.8), 363 (0.7), 320 (9.4), 263 (2.8), 237 (41.5), 219 (12.9), 193 (24.5), 165 (21.4), 129 (4.5), 101 (21.0), 83 (100), 77 (1.3), 69 (18.7), 55 (23.0).

$[(Me_4C_2O_2)BC(C_{10}H_7)B(O_2C_2Me_4)]$, 5b: 75% (0.58 g) yield, mp 91 °C. ^{1}H NMR ($CDCl_3$): δ 1.21 (s, 24H, CH_3), 1.73 (t, 2H, CH_2, $^3J_{H-H} = 6$ Hz), 1.93 (m, 2H, CH_2 , $^3J_{H-H} = 6.2$ Hz), 2.74 (t, 2H, CH_2 , $^3J_{H-H} = 6.2$ Hz), 6.97 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.03 (CH_2), 27.77 (CH_2), 24.50 (CH_3), 24.66 (CH_3), 33.26 (CH_2), 83.19 (CCH_3), 123.77 (CH), 124.86 (CH), 128.96 (CH), 130.45 (CH), 135.71 (C), 140.51 (C), (CB cannot be detected). ^{11}B NMR ($CDCl_3$): δ 31.88. Anal. Calcd for $C_{22}H_{34}O_4B_2$: C, 68.81; H, 8.91. Found: C, 68.23; H, 8.82. MS (EI) *m*/*z* (%): 384 (M^+, 2.1), 368 (0.6), 327 (1.8), 299 (1.0), 284 (2.0), 227 (2.5), 201 (36.3), 171 (7.62), 157 (19.7), 129 (47.9), 101 (27.4), 83 (100), 69 (19.5), 55 (18.8), 41 (18.0).

$[(Me_4C_2O_2)BC(C_6H_5)(CH_3)B(O_2C_2Me_4)]$, 5c: 76% (0.54 g) yield, mp 71 °C. ^{1}H NMR ($CDCl_3$): δ 1.22 (s, 12H, CH_3), 1.23 (s, 12H, CH_3), 1.45 (s, 3H, CH_3), 7.28 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.50 (CH_3), 24.60 (CH_3), 83.28 (CCH_3),

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[39] Almenningen, A.; Seip, H. M.; Willadsen, T. *Acta Chem. Scand.* **1969**, *23*, 2748.

[40] Abu Ali, H.; Goldberg, I.; Srebnik, M. *Eur. J. Inorg. Chem.* **2002**, 73.

[41] Miller, J. B. *J. Org. Chem.* **1959**, *24*, 560.

[42] Giri, B. P.; Prasad, G.; Mehrotra, K. N. *Can. J. Chem.* **1979**, *57*, 1157.

[43] Schönberg, A.; Kader, A. E.; Sammour, A. E. M. A. *J. Am. Chem. Soc.* **1957**, *79*, 6020.

[44] Jonczyk, A.; Wlostowska, J. *Synth. Commun.* **1978**, *8* (8), 569.

124.31 (para CH), 127.80 (ortho or meta CH), 128.17 (ortho or meta CH), 145.31 (ipso), (*C*B cannot be detected). ^{11}B NMR ($CDCl_3$): δ 32.90. Anal. Calcd for $C_{20}H_{32}O_4B_2$: C, 67.10; H, 9.01. Found: C, 67.18; H, 8.96. MS (EI) *m*/*z* (%): 358 (M^+, 3.0), 343 (1.1), 301 (1.6), 285 (0.1), 227 (1.2), 201 (1.4), 175 (11.7), 145 (2.4), 131 (10.5), 129 (2.9), 101 (12.1), 83 (100), 77 (1.5), 69 (11.4), 55 (12.4), 41 (11.7).

[($Me_4C_2O_2$)BC($CH_3OC_6H_4$)(CH_3)B($O_2C_2Me_4$)], 5d: 75% (0.58 g) yield, mp 88 °C. ^{1}H NMR ($CDCl_3$): δ 1.26 (s, 12H, CH_3), 1.27(s, 12H, CH_3), 1.35 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 6.78 (dd, 1H, CH, $^3J_{H-H} = 7.8$, $^4J_{H-H} = 0.9$ Hz), 6.85 (dt, 1H, CH, $^3J_{H-H} = 7.5$, $^4J_{H-H} = 1.2$ Hz), 7.10 (dt, 1H, CH, $^3J_{H-H} = 8.01$, $^4J_{H-H} = 2.1$ Hz), 7.24 (dd, 1H, CH, $^3J_{H-H} = 7.5$, $^4J_{H-H} = 1.5$ Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 19.06 (CH_3), 24.74 (CH_3), 54.99 (OCH_3), 82.97 (*C*CH_3), 110.26 (ortho or meta CH), 120.64 (ortho or meta CH), 126.10 (para CH), 129.71 (ortho or meta CH), 135.51 (ipso), 157 (*C*OCH_3), (*C*B cannot be detected). ^{11}B NMR ($CDCl_3$): δ 34.14. Anal. Calcd for $C_{21}H_{34}O_5B_2$: C, 65.01; H, 8.83. Found: C, 65.11; H, 8.78. MS (EI) *m*/*z* (%): 373 ($M^+ -$ 15, 2.0), 330 (12.8), 315 (9.5), 288 (51.0), 273 (22.3), 247 (6.9), 215 (24.2), 188 (14.1), 173 (17.7), 161 (19.4), 146 (26.2), 129 (27.0), 101 (21.5), 83 (100), 77 (6.83), 69 (8.5), 55 (14.4), 41 (11.2).

X-ray Crystallographic Study. Colorless single crystals of **5a**, **5b**, **5c**, and **5d** suitable for X-ray diffraction analysis were obtained from a saturated pentane solution at ca. −20 °C. The crystal data and structure refinement parameters are summarized in Table 2. All diffraction measurements were carried out on a Nonius KappaCCD diffractometer at ca. 110 K, using graphite-monochromated Mo Kα ($\lambda = 0.71070$ Å) radiation and 1° φ scans. The intensity data were integrated and scaled by the programs DENZO-SMN and Scalepack.[45] The structures were solved by direct methods (SIR-92)[46] and refined by full-matrix least-squares on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically; the hydrogens were located in idealized positions (the methyls being treated as rigid groups) and allowed to ride with thermal parameters 1.2 times those of their parent carbon.

Acknowledgment. The authors thank the Israeli Science Foundation for their support for this work.

Supporting Information Available: Tables of atomic positional and thermal displacement parameters, bond distances, bond angles, and torsion angles, together with details of data collection, structure solution, and refinement as a CIF file for compounds **5a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(45) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1996**, *276*, 307−326. *SCALEPACK*; Nonius B.V., The Netherlands, 1998.

(46) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(47) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures from Diffraction Data; University of Goettingen, Germany, 1997.